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(54) **Seamless can and a method of producing the same**

Falznahtlose Dose und sein Herstellungsverfahren

Boîte sans joint et son procédé de fabrication

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- H. Yamauchi : "Plastic Deformation and Processing", Nikkan Kogyo Newspaper, 1961.

EP 0 666 124 B1

Description

Background of the Invention

(Field of the Invention)

The present invention relates to a seamless can obtained by using a laminated material of a metal substrate and a polyester film, and to a method of producing the same. More specifically, the invention relates to a laminated seamless can wherein both the barrel portion and the bottom portion have resistance against the content and excellent flavor-retaining properties, the barrel portion exhibits excellent adhesion properties and workability, and the bottom portion exhibits excellent shock resistance (dent resistance), and to a method of producing the same.

(Description of the Prior Art)

Side seamless cans have heretofore been obtained by subjecting a metal blank such as an aluminum plate, a tin plate, a tin-free steel plate or the like plate to at one or more stages of draw working between a drawing die and a punch in order to form a cup that has a barrel portion without a seam on the side surface thereof and a bottom portion which is integrally connected to the barrel portion without forming a seam, and then, as required, subjecting the barrel portion to ironing between an ironing punch and die in order to reduce the thickness of the barrel of the container. There has further been widely known a deep-draw working according to which the side wall portion is bent and elongated along the curved corner portion of the redrawing die in order to reduce the thickness of the side wall portion (Japanese Laid-Open Patent Publication No. 501442/1981).

The method of coating a side seamless can with an organic film is represented by a method of laminating a resin film in advance on a metal blank which has not been formed, in addition to a widely accepted method of applying an organic paint onto the can that has been formed. Japanese Patent Publication No. 34580/1984 discloses the use of a material which is obtained by laminating a polyester film derived from terephthalic acid and tetramethylene glycol onto a metal blank. In producing redraw-formed cans by bend-elongation, furthermore, there has been known to use a metal plate which is coated with vinyl organosol, epoxy, phenolics, polyester, acryl or the like.

Japanese Laid-Open Patent Publication No. 101930/1991 (nearest state of the art) discloses a coated metal plate for draw-formed cans, comprising a laminated material of a metal plate, a polyester film layer of chiefly an ethylene terephthalate unit and, as required, an adhesive primer layer interposed between the metal plate and the polyester film layer, wherein the polyester film layer has an X-ray diffraction intensity ratio as defined by,

$$R_X = I_A/I_B$$

wherein I_A is an X-ray diffraction intensity by a diffraction plane which is in parallel with the polyester film surface and has a spacing of about 0.34 nm (CuKα X-ray diffraction angle of from 24° to 28°, and I_B is an X-ray diffraction intensity by a diffraction plane which is in parallel with the polyester film surface and has a spacing of about 0.39 nm (CuKα X-ray diffraction angle of from 21.5° to 24°,
of from 0.5 to 15 and has an anisotropy index of in-plain orientation of crystals of not larger than 30, as well as a thickness-reduced draw-formed can obtained by using the above coated metal plate and reducing the thickness of the side wall of barrel by bend-elongation.

By using a metal blank having a resin coating, however, the metal blank is subject to be damage by tools in the step of deep-draw-forming, in the step of deep-draw-forming for reducing the thickness and in the step of ironing working. In the portions where the coating is damaged, the metal is exposed actually or latently and is eluted or corroded at such portions. In producing seamless cans, furthermore, there takes place such a plastic flow that the size increases in the direction of height of the can but the size contracts in the circumferential direction of the can. As the plastic flow takes place, however, the adhesive force decreases between the metal surface and the resin coating and, besides, the adhesive force between them decreases with the passage of time due to strain remaining in the resin coating. Such a tendency becomes conspicuous particularly when the content is hot-canned or when the canned content is sterilized at low temperatures or high temperatures.

According to the above Japanese Laid-Open Patent Publication No. 101930/1991, cracks and pinholes are prevented from occurring even under severe conditions of deep-draw-forming, improved workability and corrosion resistance are obtained, and adhesive force between the metal blank and the coated film is not lost even when the metal blank undergoes a plastic flow, due to the fact that the polyester film layer of the laminated material has an X-ray diffraction intensity ratio (I_A/I_B) within a range of from 0.5 to 15 and, particularly, from 0.5 to 10, and has an anisotropy index of in-plain orientation of crystals of not larger than 30. It was, however, found that when the above coated metal plate is used for producing seamless cans by thickness-reducing deep-draw-forming or ironing working, there still remain problems that must be solved.

In the canned products, in practice, the bottom of the can and the coating structure in its vicinities are important. In particular, excellent dent resistance is required. This will be described below. The canned products are subjected to a practical test which is a denting test giving impact to the can to such a degree that an impact scar is formed, in order to test whether the coating of the can is maintained in a complete state even when the impact scar is formed. This is because, in practice, the canned products may often fall and receive impact or may often collide with one another. Even in such cases, the coating on the inner surfaces should not be peeled off, and defects such as cracks and pinholes should not develop. In canned products, the bottom of the can is most liable to develop impact scarring. It is therefore particularly important that the coating on the bottom portion has excellent dent resistance.

In a seamless can using a laminated material, the degree of working greatly differs between the barrel portion and the bottom portion; i.e., a large plastic flow develops in the barrel portion but the plastic flow in the bottom portion is as small as that of doming.

It was found that a can made of a laminated material having resistance against plastic flow and excellent adhesiveness and workability disclosed in the above-mentioned publication still lacks dent resistance in the bottom portion.

With the conventional deep-draw-formed cans having side wall of barrel of which the thickness is reduced by bend-elongation, the degree of reducing the thickness of the side wail of barrel portion is about 20% at the greatest. Therefore, it has been very desired to reduce the thickness of the barrel portion by 30% or more from the standpoint of decreasing the cost of metal blank and reducing the weight of the can. In order to reduce the thickness of the barrel portion, the degree of biaxial orientation of the polyester film of the laminated material must be further relaxed. When the degree of biaxial orientation is relaxed, however, the dent resistance on the bottom of the can becomes further deteriorated.

Summary of the Invention

It is therefore an object of the present invention to provide a laminated seamless can of which both the barrel portion and the bottom portion have resistance against the content and excellent flavor-retaining property, of which the barrel portion exhibits excellent adhesiveness and workability and of which the bottom portion has excellent shock resistance (dent resistance), and a method of producing the same.

Another object of the present invention is to provide a seamless can which maintains the above-mentioned excellent properties in combination even when the thickness of the barrel wall is reduced to a high degree, and a method of producing the same.

According to the present invention, there is provided a method of producing seamless cans using a laminated plate obtained by heat-adhering a polyester film onto a metal substrate, wherein a polyester (A) of the laminated plate of a portion corresponding to the bottom of the container has a biaxial orientation degree (R_X) defined by the following formula (1),

$$R_X = I_A/I_B \qquad (1)$$

wherein I_A is a diffraction intensity by a diffraction plane having a spacing of about 0.34 nm (CuKα X-ray diffraction angle is from 24° to 28°) in parallel with the polyester film surface on the bottom portion, and I_B is a diffraction intensity by a diffraction plane having a spacing of about 0.39 nm (CuKα X-ray diffraction angle is from 21.5° to 24°) in parallel with the polyester film surface on the bottom portion,

of from 2.5 to 20, a polyester (B) of a portion corresponding to the upper portion of the container barrel has a biaxial orientation degree (R_X) which is lower by at least 5% than the biaxial orientation degree of said polyester (A), and said laminated plate is formed into a cup such that H/D (H: height, D: diameter of the bottom portion) is not smaller than 1.5.

According to the present invention, furthermore, there is provided a method of producing seamless cans using a laminated plate obtained by heat-adhering a polyester film onto a metal substrate, wherein a polyester (C) of the laminated plate has a biaxial orientation degree (R_X) defined by the following formula (1),

$$R_X = I_A/I_B \qquad (1)$$

wherein I_A is a diffraction intensity by a diffraction plane having a spacing of about 0.34 nm (CuKα X-ray diffraction angle is from 24° to 28°) in parallel with the polyester film surface on the bottom portion, and I_B is a diffraction intensity by a diffraction plane having a spacing of about 0.39 nm (CuKα X-ray diffraction angle is from 21.5° to 24°) in parallel with the polyester film surface on the bottom portion.

of from 2.5 to 20, and the laminated plate is formed into a cup such that H/D (H: height, D: diameter of the bottom portion) is not smaller than 1.5 while heat-treating the barrel portion only in a step of forming the laminated plate into the cup in order to relax the monoaxial orientation of the polyester.

According to the present invention, furthermore, there is provided a seamless can obtained by forming a laminated material of a metal and a polyester film into a cup such that a final draw ratio defined by H/D (H: height, D: diameter of

the bottom portion) is not smaller than 1.5, wherein a polyester (A) on the bottom portion of the container has a biaxial orientation degree (R_X) defined by the following formula (1),

$$R_X = I_A/I_B \tag{1}$$

wherein I_A is a diffraction intensity by a diffraction plane having a spacing of about 0.34 nm (CuKα X-ray diffraction angle is from 24° to 28°) in parallel with the polyester film surface on the bottom portion, and I_B is a diffraction intensity by a diffraction plane having a spacing of about 0.39 nm (CuKα X-ray diffraction angle is from 21.5° to 24°) in parallel with the polyester film surface on the bottom portion.

of from 2.5 to 20, and a polyester (B) on the barrel portion of the container has a monoaxial orientation satisfying the following formula (2),

$$0.55 < \cos^2\phi < 1 - \exp[-0.45 I_A/I_B - 1.1\varepsilon + 0.53] \tag{2}$$

wherein $\cos^2\phi$ is an index representing the degree of monoaxial orientation of the polyester film at a portion where the barrel portion is measured, and is given by the formula (3),

$$\cos^2\phi = \frac{\int_{-90°}^{+0°} I(\phi)\cos^2\phi\, d\phi}{\int_{-90°}^{+0°} I(\phi)\, d\phi} \tag{3}$$

wherein $I(\phi)$ is an X-ray diffraction intensity at an angle ϕ by a diffraction plane (plane index of -105) having a spacing of about 0.21 nm (CuKα X-ray diffraction angle of from 41° to 45°) at right angles with the polyester film surface, ϕ is a value represented by the β -scanning angle of X-ray diffraction up to -90° presuming that the angle of structural inclination between a vector of a normal on the diffraction plane and a polyester fiber axis is zero with respect to the direction of height of the can, I_A is a diffraction intensity by a diffraction plane having a spacing of about 0.34 nm (CuKα X-ray diffraction angle is from 24° to 28°) in parallel with the polyester film surface on the bottom portion of the can, I_B is a diffraction intensity by a diffraction plane having a spacing of about 0.39 nm (CuKα X-ray diffraction angle is from 21.5° to 24°) in parallel with the polyester film surface on the bottom portion of the can, and ε is considerable strain by the processing of the laminated material at the can body measuring portion,

and preferably satisfying the following formula (4),

$$0.6 < \cos^2\phi < 0.95 - \exp[-0.45 I_A/I_B - 1.1\varepsilon + 0.53] \tag{4}$$

Brief Description of the Drawings

Fig. 1 is a plan view of a laminated plate;

Fig. 2(a) is a sectional view of the laminated plate of Fig. 1 on an enlarged scale, Fig. 2(b) is a sectional view illustrating another example;

Fig. 3 is a diagram of X-ray diffraction for explaining a method of measuring the biaxial orientation degree of a polyester;

Fig. 4 is a graph illustrating a relationship between the β -scanning angle and the diffraction intensity using a polyester film of a can barrel portion;

Fig. 5 is a graph illustrating a relationship between the monoaxial orientation index $\cos^2\phi$ and the height at portions of various heights of the can barrel portion;

Fig. 6 is a diagram explaining the generation of strain in relation to the blank and the can barrel;

Fig. 7 is a graph plotting a variety of data, wherein the abscissa represents the biaxial orientation degree I_A/I_B of polyester at the can bottom portion and the ordinate represents the monoaxial orientation index $\cos^2\phi$ of polyester at the can barrel portion;

Fig. 8 is a graph plotting a variety of data while changing the biaxial orientation degree I_A/I_B of polyester at the can bottom portion, wherein the abscissa represents the corresponding strain ε caused by the working on the can barrel portion and the abscissa represents the monoaxial orientation index $\cos^2\phi$ of polyester at the can barrel portion;

Fig. 9 is a side view showing a seamless can partly in cross section; and

Fig. 10 is a diagram explaining the deep-draw-forming for reducing the thickness.

FIG. 1

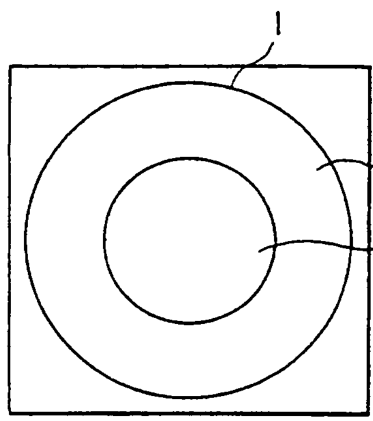


FIG. 2

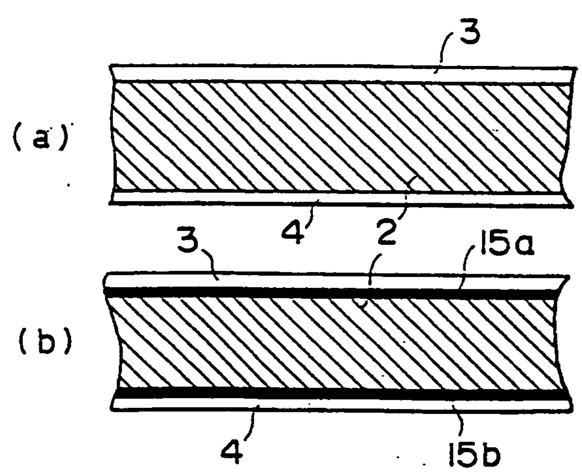
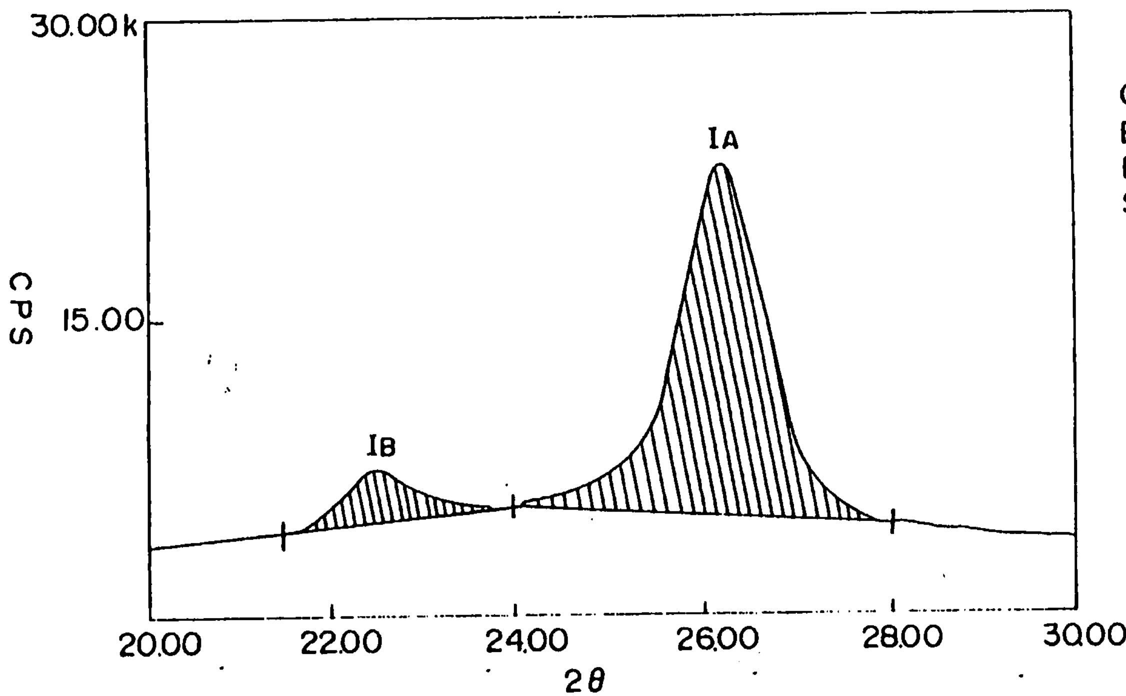


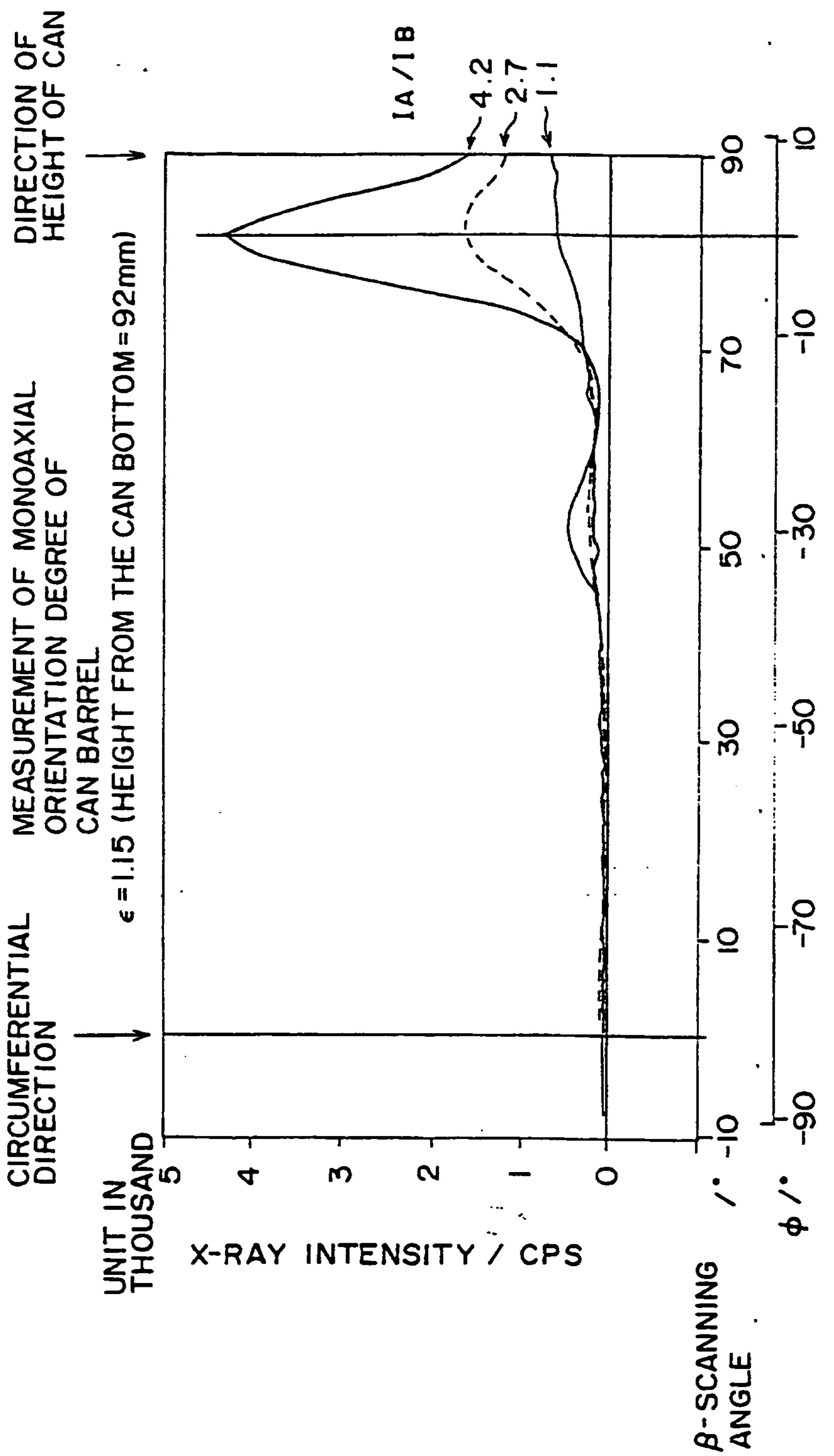
FIG. 3

CHART OF IA/IB MEASUREMENT



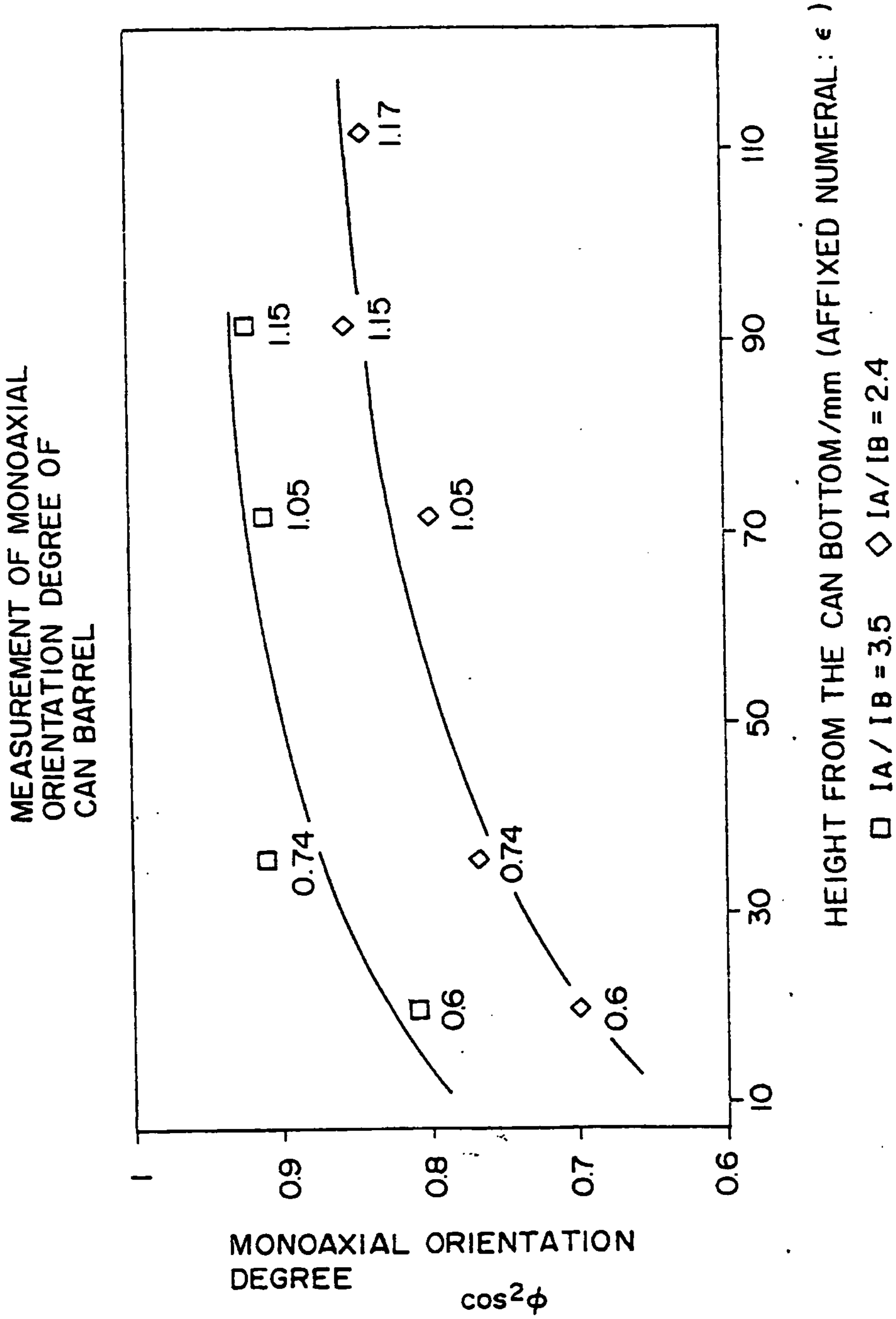
Cu TARGET
BULB VOLTAGE 30kV
BULB CURRENT 100mA
SLIT WIDTH
LIGHT-EMITTING SIDE 0.50°
LIGHT RECEIVING SIDE 0.15mm (0.05°)
SCANNING SPEED 2°/min
Ni FILTER IS USED

FIG. 4

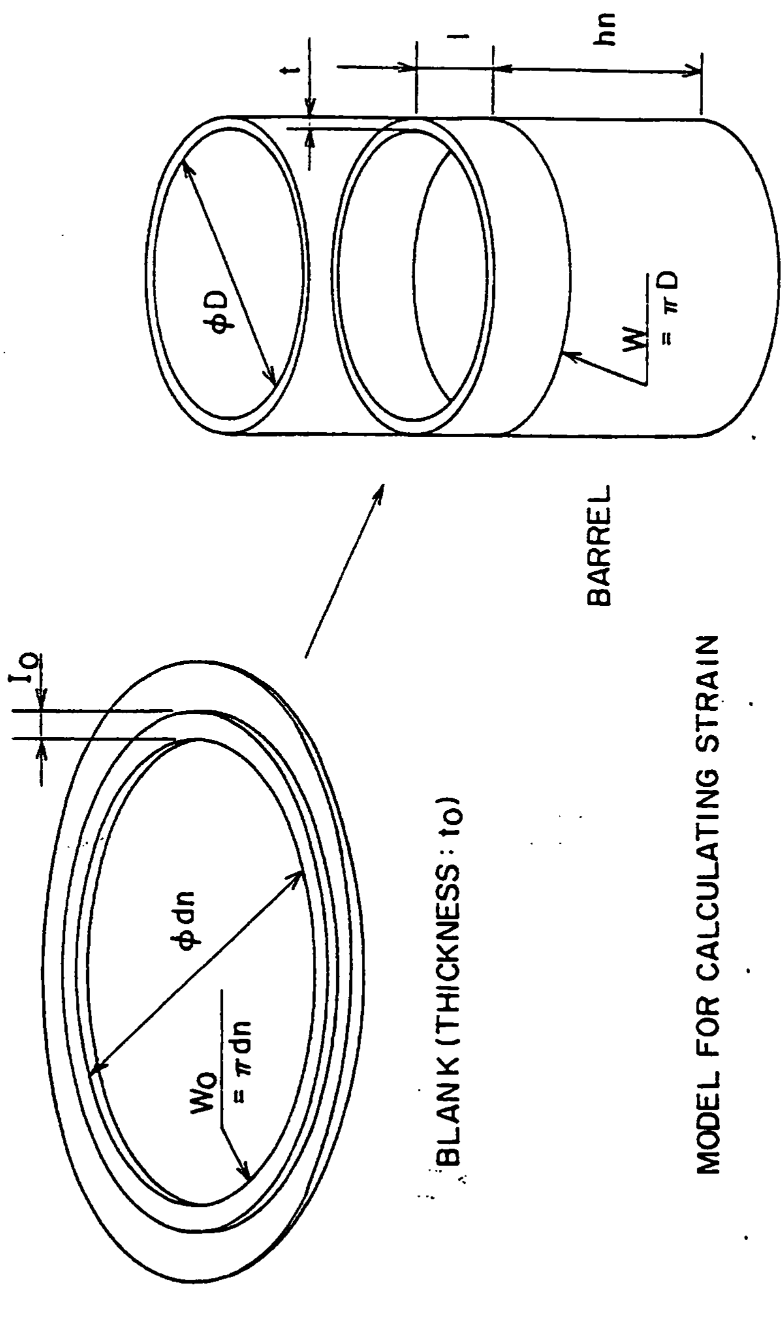


CIRCUMFERENTIAL DIRECTION
MEASUREMENT OF MONOAXIAL ORIENTATION DEGREE OF CAN BARREL
ε=1.15 (HEIGHT FROM THE CAN BOTTOM=92mm)
DIRECTION OF HEIGHT OF CAN
IA/IB
4.2
2.7
1.1
UNIT IN THOUSAND
X-RAY INTENSITY / CPS
5
4
3
2
1
0
/°
-10
10
30
50
70
90
β-SCANNING ANGLE
φ/°
-90
-70
-50
-30
-10
10

FIG. 5


MEASUREMENT OF MONOAXIAL ORIENTATION DEGREE OF CAN BARREL
MONOAXIAL ORIENTATION DEGREE
$\cos^2\phi$
1
0.9
0.8
0.7
0.6
10
30
50
70
90
110
HEIGHT FROM THE CAN BOTTOM/mm (AFFIXED NUMERAL : ε)
□ IA / IB = 3.5
◇ IA / IB = 2.4
0.6
0.74
1.05
1.15
0.6
0.74
1.05
1.15
1.17

F I G. 6



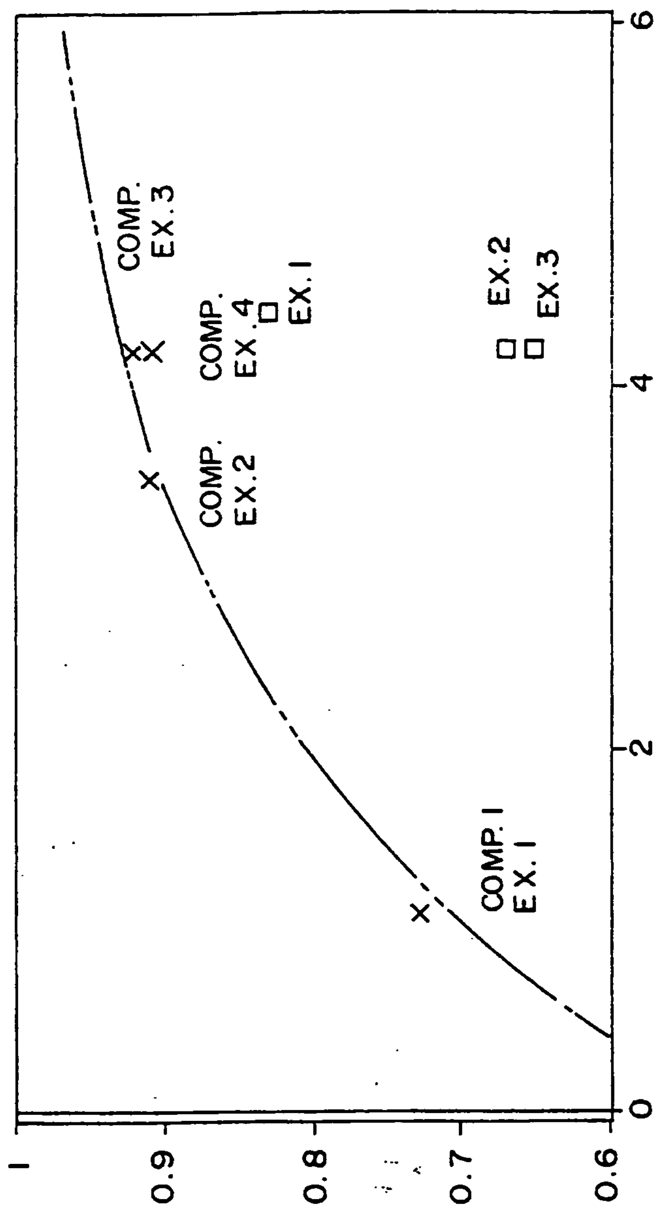
BLANK (THICKNESS: to)

BARREL

MODEL FOR CALCULATING STRAIN

FIG. 7

MONOAXIAL ORIENTATION DEGREE ON A CAN BARREL PORTION (HEIGHT = 92mm, ϵ = 1.15)



MONOAXIAL ORIENTATION DEGREE ON A CAN BARREL PORTION
$\cos^2\phi$

BIAXIAL ORIENTATION DEGREE IA / IB ON A CAN BOTTOM PORTION

□ MEASURED VALUE × MEASURED VALUE --- CURVE IN COMPLIANCE WITH EXPERIMENTAL FORMULA (6)

FIG. 8

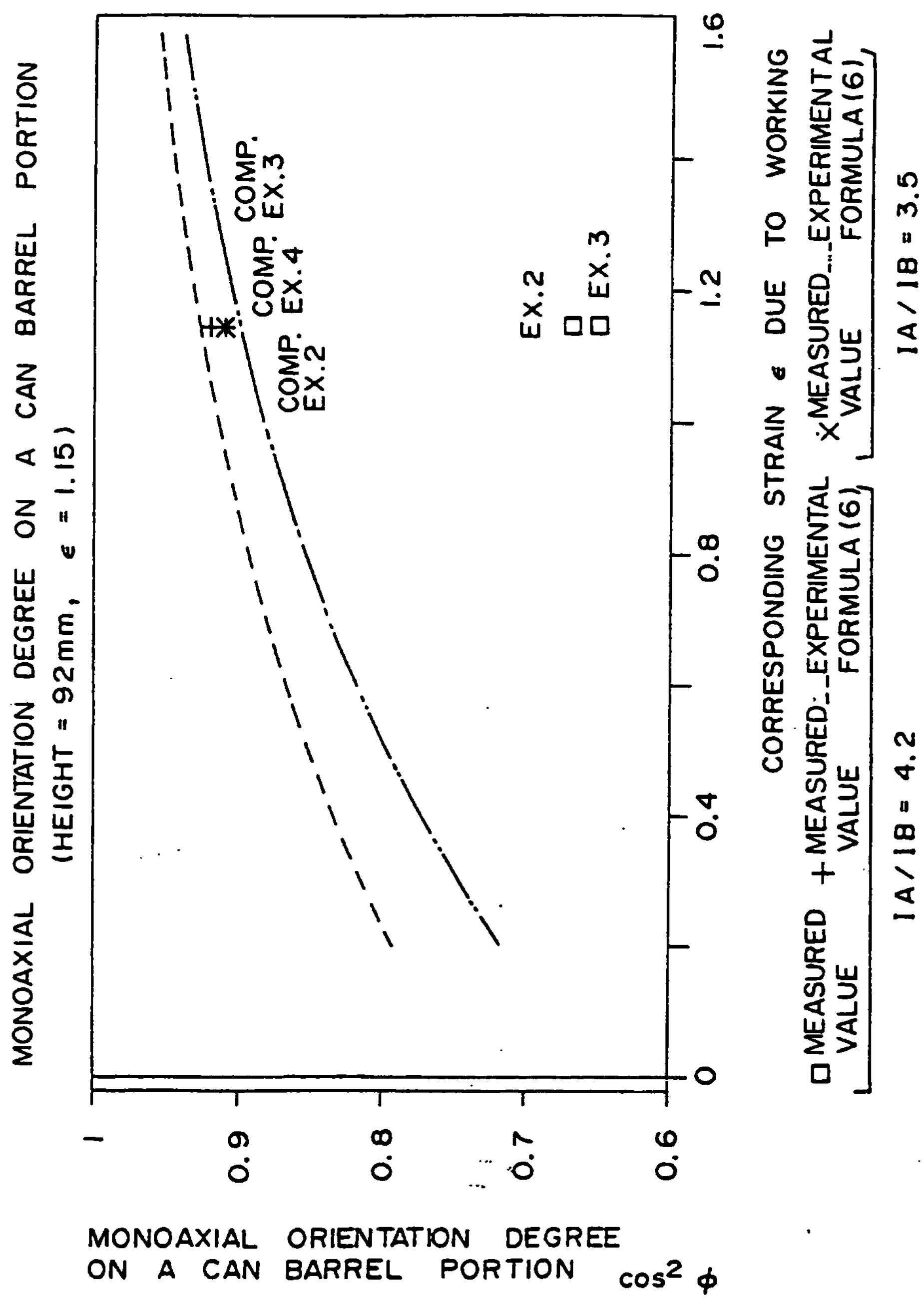

MONOAXIAL ORIENTATION DEGREE ON A CAN BARREL PORTION
(HEIGHT = 92mm, ε = 1.15)
COMP. EX.3
COMP. EX.4
COMP. EX.2
EX.2
EX.3
1
0.9
0.8
0.7
0.6
0
0.4
0.8
1.2
1.6
MONOAXIAL ORIENTATION DEGREE ON A CAN BARREL PORTION cos² φ
CORRESPONDING STRAIN ε DUE TO WORKING
□ MEASURED VALUE
+ MEASURED VALUE
-- EXPERIMENTAL FORMULA (6)
IA / IB = 4.2
× MEASURED VALUE
-·- EXPERIMENTAL FORMULA (6)
IA / IB = 3.5

FIG. 9

DEEP-DRAW-FORMED CAN (10) FOR REDUCING THICKNESS ACCORDING TO THE INVENTION

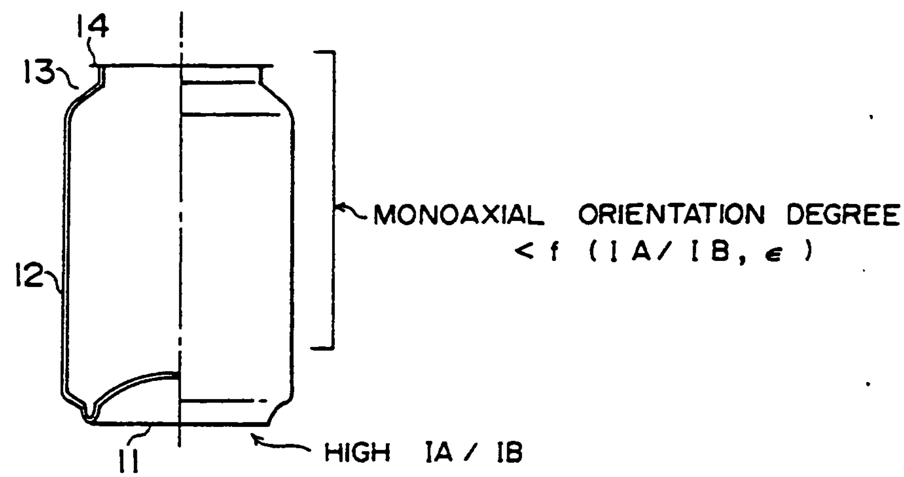


FIG. 10